

PATENT COOPERATION TREATY

PCT

REC'D 29 APR 2004

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


Applicant's or agent's file reference TS 1175 PCT	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP 03/00338	International filing date (day/month/year) 14.01.2003	Priority date (day/month/year) 14.01.2002
International Patent Classification (IPC) or both national classification and IPC B01D53/14		
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. ...		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.
 - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 3 sheets.

- This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 16.07.2003	Date of completion of this report 23.04.2004
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Bogaerts, M Telephone No. +31 70 340-2335



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/00338**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17):*

Description, Pages

1-9 as originally filed

Claims, Numbers

1-16 received on 19.11.2003 with letter of 19.11.2003

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to report.)

6. Additional observations, if necessary:

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**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-16
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-16
Industrial applicability (IA)	Yes: Claims	1-16
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP03/00338

Ad V

Reference is made to the following documents:

D1: WO-A-0066249

D2: US-A-5820837

1. The present application does not meet the requirements of Article 33(3) PCT, because the subject-matter of claims 1 and 15 does not involve an inventive step.
- 1.1 D1 (page 1, lines 1-4; page 3, line 15 - page 4, line 11; claims 1,11) discloses a process for removing acid gases such as CO₂, H₂S and COS from gas streams (e.g. natural gas), where the process uses an absorbent composition comprising an aqueous solution of MDEA and piperazine. The absorbent composition may further contain sulfolane. A specific absorbent composition comprises greater than 1 mole of piperazine per litre of aqueous solution and from 1.5 to 6 moles of MDEA per litre of aqueous solution.

The relative amounts of water, sulfolane, secondary or tertiary amine (eg MDEA) and primary or secondary amine (piperazine) specified in claim 1 are not disclosed by D1.

The objective problem is the provision of an improved process for removing acid gases as mentioned above, from gas streams, using aqueous absorbents containing both chemical and physical types of solvent.

In the absence of comparative examples it is not clear whether the relative amounts of water, sulfolane and secondary or tertiary amine as claimed in claim 1 contribute to the solution of the problem set out in the description.

Example 1 of the present application demonstrates that the addition of piperazine to an absorbent composition comprising water, sulfolane and MDEA leads to an improved removal of CO₂ from a gas stream. The effect of the addition of piperazine is known from D1. The subject-matter of claim 1 is therefore not inventive.

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- 1.2 The same arguments apply, mutatis mutandis, with respect to claim 15.
2. The features of dependent claims 1-13 and 16 are either known or directly derivable from D1.
3. The features of claim 14 do not appear to contribute to the solution of the problem set out in the description. Furthermore they are well known in the art (see eg D2, column 2, line 55 - column 5, line 54).

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C L A I M S

1. Process for the removal of carbon dioxide and optionally hydrogen sulphide and/or COS from a gas stream containing these compounds by washing the gas with an aqueous washing solution containing between 15 and 45 parts by weight based on total solution of water, between 15 and 40 parts by weight based on total solution of sulfolane and between 30 and 60 parts by weight based on total solution of a secondary or tertiary amine derived from ethanol amine, the amounts of water, sulfolane and amine together being 100 parts by weight, the process being carried out in the presence of a primary or secondary amine compound in an amount between 0.5 and 15 wt% based on water, sulfolane and amine.
2. Process according to claim 1, in which the gas stream is natural gas or synthesis gas.
3. Process according to claim 1 or 2, in which the amount of carbon dioxide is between 1 and 45 mol%, preferably between 5 and 25 mol%, the amount of hydrogen sulphide is between 0 and 25 mol%, preferably between 0 and 10 mol%, and the amount of COS is between 0 and 2 mol% (all % based on total gas stream).
4. Process according to any of claims 1 to 3, in which the amount of water is between 20 and 45 parts by weight, the amount of sulfolane is between 20 and 35 parts by weight and the amount of amine is between 40 and 55 parts by weight, the amounts of water, sulfolane and amine together being 100 parts by weight.

5. Process according to any of claims 1 to 4, in which the secondary amine derived from ethanolamine is DIPA, DEA or MMEA, preferably DIPA.
6. Process according to any of claims 1 to 4, in which the tertiary amine derived from ethanolamine is MDEA or DEMEA, preferably MDEA.
7. Process according to any of claims 1 to 6, in which the primary or secondary amine compound has a pK_b (at 25 °C in water) below 5, preferably below 4.5.
8. Process according to any of claims 1 to 6, in which the primary or secondary amine compound reacts at least twice as fast with carbon dioxide then the amine reacts with carbon dioxide, the reaction velocity defined by the reaction velocity constant (at 25 °C), the primary or secondary amine compound preferably reacting five times as fast as the amine, more preferably reacting twenty times as fast as the amine.
9. Process according to any of claims 1 to 8, in which the primary or secondary amine compound is piperazine, methyl ethanol amine, or (2-aminoethyl)ethanol amine, especially piperazine.
10. Process according to any of claims 1 to 9, in which the amount of primary or secondary amine compound is between 2.5 and 10 wt%.
11. Process according to any of claims 1 to 10, in which the amount of primary or secondary amine compound is at least 0.8 mol/l, especially between 1.0 mol/l and 3.0 mol/l, more especially between 1.0 mol and 3.0 mol piperazine/l.
12. Process according to any of claims 1 to 11, in which the process is carried out at a temperature of at least 20 °C, preferably between 25 and 90 °C, more preferably

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between 40 and 65 °C at a pressure between 25 and 90 bara.

13. Process according to any of claims 1 to 12, which process also comprises a regeneration of the loaded solvent.

14. Process according to any of claims 1 to 13, in which the process is carried out a pressure between 25 and 90 bara, in which process the loaded solvent is flashed of at a pressure between 1 and 15 bara, followed by regeneration at a pressure between 1 and 2 bara.

15. An absorbent liquid containing between 15 and 45 parts by weight based on total solution of water, between 15 and 40 parts by weight based on total solution of sulfolane and between 30 and 60 parts by weight based on total solution of a secondary or tertiary amine derived from ethanol amine, the amounts of water, sulfolane and amine together being 100 parts by weight and a primary or secondary amine compound in an amount between 0.5 and 15 wt% based on water, sulfolane and amine.

16. An absorbent liquid as defined in claim 15, the individual compounds further defined as in claims 4, 5, 6, 7, 8, 9, 10 or 11

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